

(19)



Europäisches Patentamt

European Patent Office

Office européen des brevets



(11)

EP 0 741 146 A1

(12)

EUROPEAN PATENT APPLICATION

(43) Date of publication:
06.11.1996 Bulletin 1996/45

(51) Int. Cl.⁶: **C08F 10/02**, C08F 4/607,
C08F 4/611

(21) Application number: **96106289.0**

(22) Date of filing: **22.04.1996**

(84) Designated Contracting States:
AT BE CH DE DK ES FR GB GR IE IT LI LU NL SE

(30) Priority: **05.05.1995 IT MI950896**

(71) Applicant: **ENICHEM S.p.A.**
I-20124 Milano (IT)

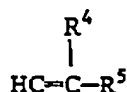
(72) Inventors:
• **Fusco, Roberto**
Novara (IT)

• **Longo, Luca**
Novara (IT)
• **Gila, Lilliana**
28063 Cameriano (NO) (IT)
• **Cambisi, Franco**
Novara (IT)

(74) Representative: **Gennari, Marco**
Eniricerche S.p.A.,
BREL,
Via F. Maritano, 26
20097 San Donato Milanese (MI) (IT)

(54) **Catalyst with improved activity for ethylene (co)-polymerization**

(57) An improved process for ethylene (co)polymerization is carried out in the presence of a catalyst obtained by reacting a Ziegler-Natta catalyst, or a component thereof, wherein at least a transition metal is π -bonded to an organic residue, with an alpha-olefin having the following general formula (II):



(II)

wherein R^4 and R^5 are two substituents selected, independently, from linear, cyclic or branched aliphatic or aromatic hydrocarbon groups having from 1 to 12 carbon atoms, or they are linked to each other to form a substituted or non-substituted cyclic compound, comprising the vinyl carbon atom in a ring of from 3 to 8 carbon atoms.

The polymerization process allows productivity values to be obtained which are higher than those obtained with an analogous process carried out without the preliminary interaction with the above said alpha-olefin, while simultaneously allowing a complete freedom with regard to the choice of the monomer composition.

EP 0 741 146 A1

Description

The present invention relates to a catalyst with improved activity for ethylene (co)polymerization.

More particularly, the present invention relates to a Ziegler-Natta catalyst particularly active in processes for ethylene homopolymerization or (co)polymerization with other α -olefins.

In general, it is known in the art that it is possible to (co)polymerize ethylene by means of low, medium and high, pressure processes, with transition metal-based catalysts, generally known as Ziegler-Natta catalysts.

The catalysts useful for such a purpose, which may be either homogeneous or heterogeneous, are generally obtained by contacting a precursor species constituted by a transition metal compound, preferably belonging to groups (IVB) e (VB) of the Periodic Table of the elements, with a co-catalyst constituted by an organometallic compound or a hydride of metals belonging to groups (IA), (IIA) or (IIIA) of said Periodic Table, by operating in suspension, in solution, or also in the absence of solvents or diluents. For such a technique reference is made to the disclosure by J. Boor in "Ziegler-Natta Catalysts and Polymerization", Academic Press, New York (1979). However, cases exist in which an organometallic compound of a transition metal proved to be active in olefins polymerization also in the absence of said co-catalyst, as disclosed, for example, in Italian Patent Applications N. 22075 A/90 and N. MI92A00415.

A particular class of said catalysts active in ethylene (co)polymerization are obtained by combining an oxygen containing organo-aluminium derivative (commonly referred to as an "aluminoxane") with an η^5 -cyclopentadienyl derivative of a metal such as titanium, zirconium or hafnium, also commonly referred to as "metallocene", which, in its most general form, can be defined by the following formula (I):



wherein

-- M represents a metal belonging to group (IVB) of the Periodic Table of the elements, formally in oxidation state +4, and preferably is titanium or zirconium;

-- R¹ and R² represent, each independently, a group of anionic character such as, for example, a hydride, a halogenide, a phosphonate or sulfonate anion, an alkyl or alkoxy group, an aryl or aryloxy group, an amide group, a silyl group, and so forth;

-- C_p represents, independently, an η^5 -cyclopentadienyl ligand and is generally selected among η^5 -cyclopentadienyl, η^5 -indenyl, η^5 -fluorenyl and variously substituted derivatives thereof;

-- R³ can have, independently from the nature of the other substituents, one of the meanings of the ligand C_p and of R¹ or R² groups. "Bridge" metallocene compounds, wherein two groups C_p, which may be the same or different from each other, are bonded by a covalent bridge which usually comprises also other carbon atoms or heteroatoms, also resulted to be particularly interesting in the prior art. For a known technique for the preparation of the above said compounds, reference is made, for exemplifying purposes, to H. Sinn, W. Kaminsky, in Adv. Organomet. Chem., Vol. 18 (1980), page 99 and to U.S. Patent No. 4,542,199.

Also other classes of compounds are known in the art which are suitable for preparing Ziegler-Natta catalysts, such as, for example, organometallic derivatives which can be referred to as "metallo-arenes", in which an aromatic group (arene) is " π "-bonded to a transition metal preferably selected among metals belonging to the groups from IVB to IVB of the Periodic Table. Such metallo-arenes are capable, when combined with an aluminium organometallic derivative, of polymerizing olefins.

A large number from said catalysts, both homogeneous and heterogeneous, are characterized by high polymerization activities and allow high productivity levels to be reached. However, the increased field requirements as well as the need for further decreasing the metal content in the so obtained polyethylene, involve a continuous research work for catalysts and polymerization processes characterized by still higher activity and productivity levels.

Among the various solutions proposed, from the specific literature of the technical field, several references describe, and variously interpret, the activating effect of an α -olefin on ethylene polymerization in the presence of the above-said, both homogeneous and heterogeneous, catalysts. It was observed, in fact, that ethylene polymerization takes place more rapidly in the presence of a comonomer selected among α -olefins. In particular, investigations can be cited which relate to the activating effect of 1-butene or 1-hexene with "classic" catalysts, obtained by starting from titanium trichloride and an electron-donor compound (Lewis base), in combination with trialkyl-aluminium

compounds (V. Pasquet et al., in "Makromolekulare Chemie", Vol. 194 (1993), pages 451-461). A work relating to the activating effect of 4-methyl-1-pentene with analogous catalysts is reported by P. J. T. Tait et al. in "Proceedings of the International Symposium on Catalyst Design for Tailor-Made Polyolefins", Kanezawa, March 10-12, 1994, K. Soga and M. Terano editors, Elsevier Publisher, (1994), pages 55-72.

The activating effect was also described of alpha-olefins in ethylene polymerization by means of catalysts belonging to the most recent "generation", based on metallocenes, such as, for example, in the paper by J. Koivumaki et al., in "Macromolecules", Vol. 27 (1994), pages 6254-6258, relating to 1-dodecene and 1-octadecene comonomers. However, the alpha-olefins effect on the latter catalyst type, is under discussion, and is generally low. In some cases even deactivating effects have been observed, as reported, for example, in the paper by J. C. W. Chien et al., in "J. of Polymer Science, Part A, Polymer Chemistry", Vol. 31, (1993), pages 227-237, with regard to 1-hexene.

In U.K. Patent N. 1,281,932, a considerable activating effect is reported of propylene in the presence of a catalyst based on TiCl_3 and trialkyl-aluminium compounds, whilst comparison tests carried out with internal olefins, or with 2-alkyl-substituted alpha-olefins (isobutene) did not show any meaningful improvements as compared to ethylene homopolymerization reaction carried out under the same operating conditions. Substantially analogous results, for "internal" olefins used in combination with a heterogenous catalyst, are reported by J. C. W. Chien et al., in the above cited paper.

The improvement in ethylene polymerization rate, which can be obtained in the presence of alpha-olefins results to be also affected by at least a further considerable drawback, consisting in the fact that in such processes it is not possible to prevent alpha-olefin from not being copolymerized with ethylene. Therefore, polyethylene homopolymeric cannot be obtained by means of said processes, nor is it possible to control the amount of copolymerized alpha-olefin independently from the overall process productivity. Furthermore, the activating effect of alpha-olefins on metallocene-based catalysts appears to be poorly meaningful and is at issue.

Therefore, the need persists still of having available Ziegler-Natta catalysts (or, more generally, coordination catalysts) characterized by very high activity in ethylene (co)polymerization, without incurring additional drawbacks and with the capability of obtaining polymers having the desired monomer composition being kept unchanged.

The Applicant has surprisingly found now that the activity of particular Ziegler-Natta catalysts can be considerably improved by modifying them with particular vinyl compounds.

A first object of the present invention is therefore an improved catalyst active in ethylene polymerization or in ethylene (co)-polymerization with an alpha-olefin, characterized in that it comprises the following components, into contact with each other:

(A) an alpha-olefin having the following general formula (II):



wherein R^4 and R^5 are two substituents selected, independently, from linear, cyclic or branched aliphatic or aromatic hydrocarbon groups having from 1 to 12 carbon atoms, or they are bonded to each other to form a cyclic, substituted or non-substituted, compound comprising the vinyl carbon atom in a ring containing from 3 to 8 carbon atoms, and

(B) a compound of a metal M selected from the group consisting of transition metals and lanthanides, which can be used as the catalyst or as a precursor of a catalyst capable of polymerizing ethylene in the absence of the above (A) component, which consists of, or is obtained from, an organometallic π -derivative of said metal M.

A second object of the present invention is a process for improving the activity of a Ziegler-Natta catalyst for ethylene (co)polymerization which consists of, or is derived from, an organometallic derivative of a metal M as defined above, characterized in that said catalyst is brought into contact with an alpha-olefin having the above formula (II), in such amounts that the alpha-olefin moles/M gram-atoms ratio is not lower than 2, and preferably is comprised within the range of from 50 to 500.

A further object of the present invention is an improved process for ethylene (co)polymerization, characterized in that it is carried out in the presence of the above said improved Ziegler-Natta catalyst.

By the term "ethylene (co)polymerization", as used in the following disclosure of the present invention and in the appended claims, reference is made to ethylene homopolymerization as well as to ethylene (co)polymerization with alpha-olefins such as, for example, propylene, 1-butene, styrene, 1-octene, and so forth.

In the widest meaning of the present invention, the alpha-olefin of formula (II), previously defined as the (A) component, can be any primary olefin having two hydrocarbon groups bonded to the same vinyl carbon atom. The R⁴ and/or R⁵ groups can be constituted by a linear or branched aliphatic alkyl group having from 1 to 12 carbon atoms, or by cycloalkyl or polycycloalkyl group, saturated or unsaturated, having from 4 to 12 carbon atoms, or by an aryl or arylalkyl group having from 6 to 12 carbon atoms, or, still, by a heterocyclic group having from 4 to 12 carbon atoms.

Examples of R⁴ and R⁵ aliphatic groups are methyl, ethyl, butyl, octyl, 4-methylpentyl, cyclopentyl, cyclohexyl groups, and the like. Examples of R⁴ and R⁵ aryl or arylalkyl groups are phenyl, dimethylphenyl, chlorophenyl, methoxyphenyl, benzyl, methylbenzyl groups, and the like.

Examples of heterocyclic R⁴ and R⁵ groups are furyl, pyridyl, pyrrolidino, and the like.

Olefins of formula (II) in which R⁴ is methyl or ethyl and R⁵ is selected from the group consisting of methyl, ethyl, n-propyl, n-cyclobutyl, cyclopentyl or phenyl, are preferred. Other preferred olefins according to the present invention are those in which R⁴ and R⁵ are bonded to each other to form a ring comprising the vinyl carbon atom. Examples of such olefins are: methylenecyclopentane, methylenecyclohexane, 1-methyldene-4-methylcyclohexane, 4-methyldene-norborn-1-ene.

Olefins of formula (II) particularly preferred for the purposes of the present invention are: isobutene, 2-methylpent-1-ene, 2,4-dimethylpent-1-ene, alpha-methylstyrene, methylenecyclopentane and 2-ethyloct-1-ene.

The catalyst for ethylene (co)polymerization according to the present invention comprises the (A) alpha-olefin previously defined, kept into contact with a (B) component containing a metal M as defined above, which, as such, or in combination with compounds other than (A), is capable of polymerizing ethylene. The contact between the (A) and (B) components, and possibly other components which will be defined in the following, can cause a chemical reaction to take place involving the formation, at least partially, of different compounds than those initially put into contact and previously mentioned, which, however, have to be considered fully included within the scope and the meaning of the present invention.

Said metal M can be any transition metal belonging to groups from (IIIB), to (VIIB), preferably from (IVB) to (VIB), of the Periodic Table of the elements, or it can be a metal belonging to the group consisting of lanthanides having atom number comprised within the range of from 57 to 71, such as La, Nd, Eu, and so forth.

More preferably, the metal M is Ti, Zr, Hf, V, Cr or Ni. Particularly preferred are titanium, zirconium and hafnium.

Said (B) component is itself of organometallic nature, and is constituted, or is obtained by starting from, an organometallic derivative of the metal M. In the most general form of the present invention, such an organometallic derivative of metal M is any compound, which preferably can be represented by a defined chemical formula, wherein each M is π -bonded to at least an organic residue. According to the present invention, the term "defined chemical formula" relates to those compounds which can be homogeneously represented by a single structural formula.

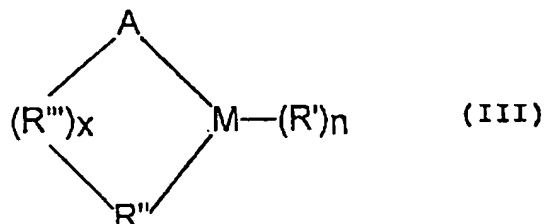
In its most general definition, the term "organic residue" relates, according to the present invention, to those organic groups having anionic, uni- or polyvalent, or even neutral, nature, possibly comprising, besides carbon, also one or more heteroatoms, which are bonded to the transition metal by means of coordination and/or delocalized bonds of π -type. Preferably, the organic residues bonded to metal M contain from 3 to 20 carbon atoms, more preferably, from 3 to 12 carbon atoms. Among the organometallic derivatives in which one or more organic residues are bonded to the metal M by means of at least one " π "-type bond, typical non-limitative examples are β -diketonate groups, such as acetylacetonate, substituted or non-substituted cyclopentadienyl group, such as cyclopentadienyl, fluorenyl, indenyl, and so forth, π -arene groups, such as benzene, toluene, mesitylene, π -alkenyl groups, such as allyl, methylallyl or cycloalkenyl, such as cyclooctenyl.

In the case where the organic residue bonded to M has neutral character, said organic residue is preferably selected from among residues which do not contain heteroatoms, such as arene groups or conjugated or non-conjugated diene groups.

Other organic residues falling within the scope of the present invention will result evident in the following of the present disclosure.

According to a preferred embodiment of the present invention, the (B) component is constituted by, or is obtained by starting from, a metallocene organometallic derivative, in which at least an η^5 -cyclopentadienyl ligand is bonded to the transition metal M, preferably selected among Ti, Zr or Hf. Such organometallic derivatives and methods for preparing them are widely reported in specific literature references. For merely exemplifying and non-limitative purposes, we mention here the paper edited by V. Gupta in "Journal of Macromolecular Science, Rev. Macromolecular Physics, Vol. C34(3) (1994), pages 439-514.

According to the purposes of the present invention, of particular interest are those metallocene derivatives falling within the following general formula (III):



wherein:

- M represents a metal selected from transition metals belonging to groups (IIIB), (IVB), (VB) and (VIB) and from lanthanides;
- A is an anion containing an η^5 -cyclopentadienyl ring coordinated to metal M;
- each of n R¹'s represents, independently, a substituent group selected among hydride, halide, a C₁-C₈-alkyl group, a C₃-C₁₂-alkylsilyl group, a C₅-C₈-cycloalkyl, a C₆-C₁₀-aryl group, a C₁-C₈-alkoxy group, a C₁-C₈-carboxy group, a C₂-C₁₀-dialkylamide group and a C₄-C₂₀-alkylsilylamide group;
- R' represents a substituent group of the same type as the preceding R' groups, selected independently from them, or a second anion containing an η^5 -cyclopentadienyl ring coordinated to metal M;
- R'' represents a bivalent group having from 1 to 10 carbon atoms, possibly containing one or more heteroatoms, preferably, O, N, P, or Si, which is bridge-bonded between A and R' by means of a covalent bond. R'' is preferably selected from alkylene, dialkylsilylene, diarylsilylene, alkyl- or arylamino or phosphino radicals, arylene, and the like.
- "n" is an integer number and is equal to the valency of M minus 2;
- "x" can be either 0 or 1.

In the compounds having the above formula (III), when "x" is 0 both groups R'' and A are not bridge-bonded to each other. Typical non-limitative examples of R'' are methylene, 1,2-ethylene, dimethylsilylene groups.

The metal M in the compound of formula (III) is preferably selected from titanium, zirconium, hafnium, vanadium and chromium, more preferably titanium and zirconium.

According to the present invention, the groups R' of formula (III) can represent, each independently, a hydride or halide, such as chloride or bromide, a C₁-C₈-alkyl group such as, for example, methyl, ethyl, butyl, isopropyl, isoamyl, octyl, benzyl, a C₃-C₁₂-alkylsilyl group such as, for example, trimethylsilyl, triethylsilyl or tributylsilyl, a cycloalkyl group, such as cyclopentyl or cyclohexyl, a C₆-C₁₀-aryl group such as phenyl or tolyl, a C₁-C₈-alkoxy group such as, for example, methoxy, ethoxy iso- or sec.-butoxy, or, furthermore, a C₂-C₁₀-dialkylamide or C₄-C₂₀-alkylsilylamide group, preferably of the type which can be represented by the general formula -NR⁴R⁵, wherein R⁴ and R⁵ are alkyl groups having from 1 to 4 carbon atoms, such as, for example, methyl, ethyl or butyl groups, or, in the case of alkylsilylamides, alkylsilyl groups having from 3 to 6 carbon atoms, such as, for example, trimethylsilyl or triethylsilyl.

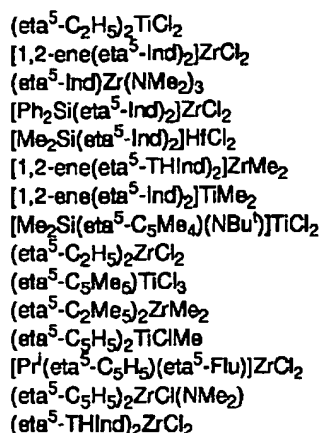
Preferably, R' groups of formula (III), represent a radical selected among chloride, methyl, benzyl and diethylamino. In a particularly preferred embodiment, the R' groups are all equal to one another.

According to the present invention, the A group in formula (III) is an anion containing an η^5 -cyclopentadienyl ring which is preferably derived (formally by extraction of an H⁺ ion) from a cyclopentadiene, indene or fluorene molecule, or from a derivative of the above said compounds, wherein one or more carbon atoms of the molecular backbone (comprised or not comprised within the cyclopentadienyl ring), are substituted by C₁-C₈-alkyl or silylalkyl groups, or C₆-C₁₀-aryl or aryloxy, or C₁-C₈-alkoxy. Said A group can also be condensed with one or more other aromatic rings such as in the case of, for example, 4,5-benzoindenyl. Particularly preferred A groups are indenyl groups, 4,5,6,7-tetrahydroindenyl and the corresponding methyl-substituted groups.

As defined above, R'' in formula (III) can represent both a group falling within the above meaning of the R' group, as well as a group falling within the above meaning of A group. When "x" = 1, the R'' group is bonded to the A group by means of the R''' bridge; in such case it will clearly represent a group falling within the meaning of R' or, respectively, A, but having a position substituted by the bond with the R''' bridge.

Metallocenes having the above formula (III) are generally known in the art and can be prepared by means of one of the usual suitable methods, described in manuals relating to organometallic compounds synthesis, or in the wide field of patent literature relating to the use of metallocenes in olefins polymerization. For exemplifying purposes, reference is made again to the paper by V. K. Gupta, previously cited, as well as to patent publications N. EP-A-416 815, N. EP-A-528 287, N. EP-A-574 794, N. EP-A-576 970, N. EP-A-577 581, WO Patent N. 86/05788, U.S. Patent N. 5 264 405 and U.S. Patent N. 5 304 523.

Non-limitative examples of compounds of formula (III) are reported in the following:



In the preceding formulae the following abbreviations were used: Me = methyl, Et = ethyl, Bu^t = tert.-butyl, Bz = benzyl, Prⁱ = 2,2-isopropylidene, Ind = indenyl, THInd = 4,5,6,7-tetrahydro-indenyl, Flu = fluorenyl, 1,2-ene = 1,2-ethyldiene, Ph₂Si = diphenylsilylene, Me₂Si = dimethylsilylene.

Further suitable metallocenes for the purposes of the present invention, not comprised within the above formula (III) are the so-called (cationic metallocene systems which usually comprise compounds containing one single A type cyclopentadienyl anion coordinated to metal M, with the latter preferably being titanium, zirconium and hafnium. Said cationic metallocenes are characterized by the presence of a positive charge on the metal M complex, and by a non-coordinating counter-anion such as, for example, tetrafluoroborate or tetraphenylborate. Such typical metallocenes and methods for obtaining them are described, for example, in published patent applications N. EP-A-495 375, N. EP-A-520 732, N. EP-A-478 913 and WO 92/00333.

According to a second embodiment of the present invention, the (B) component is constituted by, or is obtained by starting from, those metallo-arenes which are capable, either as such or in combination with other compounds, of forming active catalysts in olefins polymerization. Metallo-arenes are compounds characterized by the presence of a neutral arene ligand coordinated to the metal M selected from the transition metals. Compounds belonging to such group are described, for example, in U.S. Patent 498 491. Further metallo-arenes useable for the purposes of the present invention are reported, for example, in European Patent Application N. EP-A-604 855.

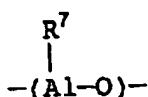
Those (B) components fall furthermore within the scope of the present invention, which are constituted by, or are obtained by starting from, a metallocene or a metalloarene belonging to any of the preceding classes previously described, which is supported on a solid inert carrier, preferably selected from the inert inorganic oxides, more preferably selected from alumina, silica, and aluminosilicates. Such supported complexes can be obtained by impregnating the carrier by means of a solution of the metal complex in an inert solvent, or they can be prepared by means of methods comprising the formation of relatively stable chemical bonds between complex and carrier. Supported metallocene complexes or metalloarenes, active in olefins polymerization, and methods for the preparation thereof, are described in a number of papers generally known to those skilled in the art, such as, for example, Italian Patent Application N. 95/A 000167, European Patent Application publication Nos. EP-A-442 725 and EP-A-516 458, and U.S. Patent N. 5 057 475.

The (B) component as defined above is not necessarily represented by a specific structural formula. In fact, it can also be constituted by compounds having not defined stoichiometry and structure, but obtained by means of specific processes, with the proviso that, in the most general form thereof, it contains at least a portion, preferably from 50 to 100 %, of metal M bonded to one or more organic residues by covalent "π"-type bonds.

Besides (A) and (B) components, the catalyst according to the present invention can comprise, if necessary or however desirable for an optimal implementation of the same invention, all other usual typical components of Ziegler-Natta catalysts known in the art, which are normally required in order to activate the only (B) component in ethylene polymerization. In particular, the catalyst of the present invention can comprise, when so required, a third (C) component constituted by a hydride or an alkyl-derivative of a metal M', preferably selected from alkali metals, alkaline-earth metals, aluminium, gallium or tin.

More particularly, said (C) component is preferably constituted by an aluminoxane in the case where the (B) component comprises a metallocene derivative. It is well known that aluminoxanes are compounds containing Al-O-Al bonds, with variable O/Al ratios, which can be obtained in the art by reacting, under controlled conditions, an alkylaluminum compound, or alkylaluminum halogenide, with water or other compounds contained controlled amounts of available water, such as, for example, in the case of trimethylaluminum, with a hydrous salt, such as aluminium sulfate

hexahydrate, copper sulfate pentahydrate and iron sulfate pentahydrate. Aluminoxanes preferably useable for the formation of the polymerization catalyst of the present invention are cyclic or linear, oligomeric or polymeric compounds, characterized by the presence of repetitive units of formula:



wherein R^7 is a C_1 - C_4 -alkyl group, preferably methyl.

Each aluminoxane molecule preferably contains from 4 to 70 repetitive units which can also be not the same, but can contain different R^7 groups.

In particular, in ethylene polymerization catalysts of the present invention, the aluminoxane and the (B) component comprising a metallocene are used in such amounts that the atomic ratio between aluminium in aluminoxane and metal M is comprised within the range of from 10 to 10000 and preferably of from 100 to 5000.

Besides the above said aluminoxanes, within the definition of (C) component of the present invention also galloxanes (wherein, in the preceding formulae, gallium is present in place of aluminium) and stannoxanes fall. The use of stannoxanes, as cocatalysts for olefins polymerization in the presence of metallocene complexes is reported, for example, in U.S. Patent Nos. 5,128,295 and 5,258,475.

In those case where the (B) component of the catalyst of the present invention do not comprise a metallocene derivative, then, according to what is generally known in the art, said (B) component should desirably be combined with a (C) component constituted by an alkyl-metal compound or an alkyl metal halide, of a metal M' belonging to groups (IA) (IIA) or (IIIA) of the Periodic Table, preferably magnesium or aluminium, more preferably a trialkylaluminium or trialkylaluminium halide, which performs the function of cocatalyst. Each alkyl radical bonded to metal M' preferably contains from 1 to 8 carbon atoms and can be either linear or branched.

Non-limitative examples of suitable alkylmetal compounds or alkyl halides to form the (C) component of the catalyst according to the present invention are: methyl lithium, butyllithium, diethylmagnesium, ethylmagnesium chloride, trimethylaluminium, triethylaluminium, triisobutylaluminium, diethylaluminium chloride, ethylaluminium dibromide, ethylaluminium sesquichloride.

According to the present invention, the above said (B) and (c) components can be combined in the normally used ratios in the art for obtaining traditional polymerization catalysts, examples of which are widely reported in previously cited reference papers. Normally, the atomic ratios between metal M' in the cocatalyst and metal M in the organometallic derivative, are comprised within the range of from 10 to 5000, preferably of from 50 to 1000.

According to the present invention, the sequence according to which the (A), (B) and possibly (C), components are mixed with one another, is not critical. In particular, the (A) component can be combined with (B) component, and subsequently with (C) component, or (B) and (C) components can be pre-mixed and reacted with each other, with the (A) component being subsequently added to the resulting mixture.

According to the process of the present invention for the preparation of the improved ethylene polymerization catalyst, the (A) and (B) components can be mixed with each other in each of the characteristic steps of the preparation of a Ziegler-Natta catalyst. In fact, on the base of Applicant's experience, the choice of the mixing step is not critical. It is however preferable that such a mixing is carried out before that the contact between the catalytic system (i.e., the catalyst, or catalyst plus activating agent, according to the traditional terminology) and ethylene takes place, in order to obtain the maximum catalyst activation. However, those catalysts formed by introducing the olefin of formula (II) after ethylene polymerization starting in the presence of the only catalyst based on the previously defined (B) component, are not excluded from the scope of the present invention.

The mixing and contacting steps of the different components of the catalyst according to the present invention, in particular the (A) and (B) components and the optional (C) component, can be carried out within wide time and temperature ranges. (B) and (C) components are preferably mixed and kept into contact at temperatures, under conditions and during time periods which are the same as those used in the art in order to obtain the traditional desired catalyst in the absence of the (A) component. The (A) component is preferably brought into contact with the (B) component or with the resulting product from (B) and (C) for the time periods which are necessary in order to obtain the desired activation, which are normally comprised within the range of from 2 seconds to 5 minutes, at temperatures comprised within the range of from -50°C to $+150^\circ\text{C}$. Longer contact times do not produce further activity increases, but, however, it is preferable that such a contact is kept between the catalyst components at least until the polymerization step, and, possibly, also during such a step.

According to the present process for preparing the improved catalyst of the present invention, one or more components can be mixed, and possibly, reacted with the (B) component before or after the contact of the latter with the (A) alpha-olefin.

Additives or components which can be comprised within the preparation and/or formulation of the catalyst of the present invention, are inert solvents, such as, for example, aliphatic and/or aromatic hydrocarbons, aliphatic and aromatic ethers, coordinating additives (Lewis' Bases) such as, for example, ethers, tertiary amines, alcohols, phosphines, halogenating agents such as silicon halides, halogenated, preferably chlorinated, hydrocarbons, hydrochloric acid and the like, and furthermore, all such other components as normally used in the preparation of homogeneous or heterogeneous traditional Ziegler-Natta catalysts for ethylene (co)polymerization.

The catalysts according to the present invention are useful in ethylene polymerization, to yield linear polyethylene, and in ethylene (co)polymerization with propylene or higher alpha-olefins, to yield copolymers having different structures as a function of the specific polymerization conditions and of the alpha-olefin itself. The catalyst of the present invention can also be advantageously used for ethylene, propylene and a diene terpolymerization, in order to obtain vulcanizable rubbers of EPDM type. Particularly preferred is ethylene homopolymerization in the presence of said catalysts.

The catalysts according to the present invention can be used with very good results being obtained substantially in all of known polymerization processes, such as, for example, processes operating in suspension, under low, medium or high pressure and at temperatures comprised within the range of from 50 to 240°C; processes operating in solution in an inert diluent under pressures comprised within the range of from 10 to 150 bar and temperatures comprised within the range of from 120 to 230°C; or in gas phase, with temperatures generally comprised within the range of from 60 to 160°C, under pressures comprised within the range of from 5 to 50 bar. As the molecular weight regulant, hydrogen is usually used. In all cases, the catalysts according to the present invention are characterized by an evident increase in activity as compared to the activity which can be obtained without addition of (A) alpha-olefin of formula (I). Productivity increases higher than 10 %, preferably higher than 20 %, more preferably higher than 50 %, can be surprisingly obtained with the improved catalysts of the present invention. Furthermore, a considerable decrease is observed in the initial induction time period which characterizes many of the usual polymerization processes using traditional catalysts.

According to a particular aspect of the present invention, the improved catalyst for ethylene (co)polymerization is separately prepared in accordance with one of the previously mentioned methods, and is subsequently introduced in the polymerization ambient. To the polymerization reactor the catalyst can be first introduced, followed by the reacting mixture containing ethylene and eventual comonomers; or, the catalyst can be added to the reactor already containing the reacting mixture; or, finally, the reacting mixture and the catalyst can be simultaneously fed to the reactor.

According to a further aspect of the present invention, the improved catalyst is formed *in situ* in the polymerization reactor, for example, by introducing the (A) and (B) components, in which (B) is not capable, as such, of polymerizing ethylene, subsequently feeding the ethylene containing mixture and finally adding the (C) component. According to a further embodiment, the (C) component is charged to the reactor, followed by the (A) and (B) components mixture and by ethylene feed. According to a still further embodiment, the (C) component, the (A) and (B) mixture and ethylene are separately fed to the reactor and mixed therein.

According to the present invention, the (A) component can also be fed to the reactor mixed with ethylene and optional comonomers, the (B) component, or the (B) and (C) mixture, being separately fed.

The present invention is further described by the following examples, which however are reported for merely illustrative purposes, and are non-limitative of the scope of the present invention.

EXAMPLE 1

A solution consisting of a precursor of a catalyst according to the present invention is prepared by adding 1.45 ml of anhydrous 2-methyl-1-butene (distilled on calcium hydride) to a solution obtained by dissolving 21.2 mg of bis(eta⁵-cyclopentadienyl)zirconium dichloride (available from the Company FLUKA, 72.6 micromoles) in 100 ml of anhydrous toluene.

A BUCHI autoclave with one litre glass reactor, equipped with a propeller stirrer, heating resistor and temperature control jacket, was preliminarily kept under vacuum for two hours and it was then filled with nitrogen. The same cycle of vacuum/nitrogen application was repeated twice more. 500 ml of anhydrous toluene (distilled on sodium metal) and 0.54 ml of a solution consisting of 10 % by weight of methyl aluminoxane in toluene (from the Company WITCO, containing 42.4 g/litre of aluminium) were then added. The temperature was raised up to 70°C and 0.47 ml, of the previously prepared precursor solution were added. After about 5 minutes, with stirring, ethylene was charged until a pressure of 202 kPa was obtained. The polymerization started immediately and was carried out for 30 minutes by keeping the autoclave at 70°C with stirring, and continuously feeding ethylene to maintain a constant pressure value equal to the initial value. After 30 minutes, the polymerization was stopped, and the polymer was collected by precipitation with acidified methanol and subsequent washings with acetone. After drying, 26 g of polyethylene were obtained in a yield of 8.27 Kg_{PE}/g_{Zr} • kPa_(ethylene) • h. The so obtained polymer was characterized by gel-permeation chromatography according to the usual procedure used for polyethylene, using trichlorobenzene at 130°C as the solvent. The result of such measurement was:

- $M_n = 116,000$ and
 -- $M_w = 254,000$.

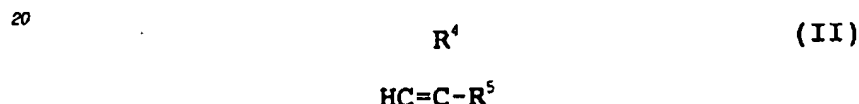
EXAMPLE 2 (Comparative example)

5 A solution of a traditional catalyst precursor is prepared by dissolving 24.0 mg of the above bis(eta⁵-cyclopentadi-
 enyl)zirconium dichloride (82.2 micromoles) in 100 ml of anhydrous toluene. An ethylene polymerization was then car-
 ried out under the same conditions as in the preceding Example 1, with the exception that 0.41 ml of the latter solution
 was used in place of the 2-methyl-1-butene containing solution. After drying, 19 g of polyethylene having average
 10 molecular weights $M_n = 134,000$ and $M_w = 270,000$, as determined as described above, in a yield of 6.37 KgPE/gZr ·
 kPa_(ethylene) · h, were obtained.

Claims

- 15 1. Catalyst for ethylene (co)polymerization, characterized in that it comprises the following components, into contact
 with each other:

(A) an alpha-olefin having the following general formula (II):



25 wherein R^4 and R^5 are two substituents independently selected from linear, cyclic or branched, aliphatic or aro-
 matic hydrocarbon groups having from 1 to 12 carbon atoms, or they are bonded to each other to form an either
 substituted or non-substituted cyclic compound comprising the vinyl carbon atom in a ring containing from 3 to
 8 carbon atoms, and

30 (B) a compound of a metal M selected from the group consisting of transition metals and lanthanides, which
 can be used as the catalyst or as a precursor of a catalyst capable of polymerizing ethylene in the absence of
 the above (A) component, consisting of, or obtained from, an organometallic derivative of said metal M, which
 contains from 50 to 100% of metal M bonded to an organic residue by means of at least a covalent π -bond.

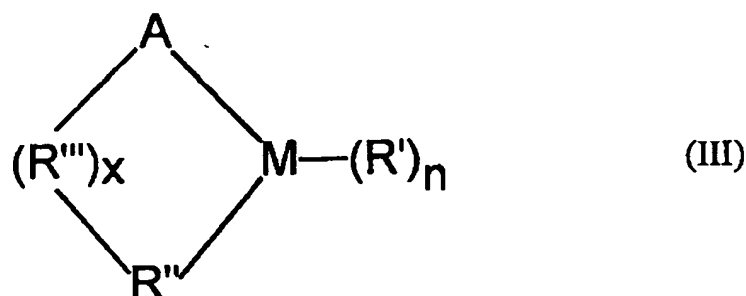
- 35 2. Catalyst according to claim 1, wherein, in said alpha-olefin of formula (II), R^4 is methyl or ethyl, and R^5 is selected
 from the group consisting of methyl, ethyl, n-propyl, n-butyl, cyclopentyl or phenyl.

3. Catalyst according to claim 1, wherein said alpha-olefin of formula (II) is selected from isobutene, 2-methylpent-1-
 ene, 2-ethylbut-1-ene, 2,4-dimethylpent-1-ene, alpha-methylstyrene, methylidenecyclopentane, methylidenecy-
 40 clohexane, 2-ethyloct-1-ene, methylidenecyclohexane, and 4-methylidenenorborn-1-ene.

4. Catalyst according to anyone of the preceding claims, in which the ratio between the moles of said alpha-olefin of
 formula (II) and the gram-atoms of said metal M is equal to, or higher than, 2, and preferably is comprised within
 the range of from 50 to 500.

45 5. Catalysts according to anyone of the preceding claims, in which said (B) component either is constituted, or is
 obtained by starting from, an organometallic derivative in which the metal M is bonded to at least one organic res-
 idue by means of at least one π -bond.

50 6. Catalyst according to claim 5, in which said organometallic derivative is a compound of metallocene type having
 the following general formula (III):



wherein:

- M represents a metal selected from transition metals belonging to groups (IIIB), (IVB), (VB) and (VIB) and from lanthanides;
- A is an anion containing at least one η^5 -cyclopentadienyl ring coordinated to the metal M;
- each of R' radicals independently represents a substituent group selected from hydride, halide, a C₁-C₈-alkyl group, a C₃-C₁₂-alkylsilyl group, a C₅-C₈-cycloalkyl group, a C₆-C₁₀-aryl group, a C₁-C₈-alkoxy group, a C₁-C₈-carboxy group, a C₂-C₁₀-dialkylamide group and a C₄-C₂₀-alkylsilylamide group;
- R'' represents a substituent group of the same nature as of the preceding R' groups, selected independently from them, or a second anion containing an η^5 -cyclopentadienyl ring coordinated to the metal M;
- R''' represents a divalent group having from 1 to 10 carbon atoms, possibly containing one or more heteroatoms, preferably, O, N, P, or Si, which is bridge-bonded between A and R'' by means of a covalent bond;
- "n" is an integer number and is equal to the valency of M minus 2;
- "x" can be 0 or 1.

7. Catalyst according to claim 6, wherein, in formula (III), "x" is 1, R''' is selected from alkylene, dialkylsilylene, diarylsilylene and arylene and R'' is a second anion containing an η^5 -cyclopentadienyl ring coordinated to metal M.
8. Catalyst according to claim 6, wherein, in formula (III), "x" is 0, and R'' is a second anion containing an η^5 -cyclopentadienyl ring coordinated to metal M.
9. Catalyst according to anyone of the preceding claims from 6 to 8, wherein the metal M of formula (III) is selected from the group consisting of titanium, zirconium and hafnium.
10. Catalyst according to the preceding claim 5, in which said organometallic derivative of metal M is a cationic metallocene system.
11. Catalyst according to the preceding claim 10, in which said metal M is selected between titanium and zirconium.
12. Catalyst according to anyone of the preceding claims from 1 to 9, comprising, besides (A) and (B) components, a third (C) component, which is into contact with them, consisting of an alkyl derivative of a metal M' selected among alkali metals, alkaline-earth metals, aluminium, gallium or tin.
13. Catalyst according to claim 12, in which said (C) component is an organo-oxygenated derivative of aluminium, gallium or tin.
14. Catalyst according to the preceding claim 13, in which said organo-oxygenated derivative is an oligomeric or polymeric methylaluminoxane containing from 4 to 70 repetitive units.
15. Catalyst according to the preceding claim 13 or 14, in which the atomic ratio between the metal in the organo-oxygenated derivative and metal M in (B) component is comprised within the range of from 10 to 10,000 and preferably of from 100 to 5,000.
16. Catalyst according to the preceding claim 12, in which said organometallic derivative of metal M is a metallo-arene or a π -allyl derivative of metal M.

17. Catalyst according to the preceding claim 16, in which said metal M is selected from titanium, zirconium or vanadium.

18. Catalyst according to anyone of the preceding claims from 16 to 17, in which said (C) component is a trialkylaluminum or an alkylaluminum halide, wherein each alkyl radical bonded to aluminium contains from 1 to 8 carbon atoms.

19. Catalyst according to the preceding claim 18, in which said alkyl radical bonded to aluminium is methyl.

20. Catalyst according to the preceding claims 18 or 19, in which the atomic ratio between aluminium in (C) component and metal M in (B) component is comprised within the range of from 10 to 5000 and preferably of from 50 to 1000.

21. Process for preparing, the catalyst according to anyone of the preceding claims from 1 to 20, characterized in that the following components are mixed with each other:

(A) an alpha-olefin having the following general formula (II):



wherein R^4 and R^5 are two substituents independently selected from linear, cyclic or branched aliphatic or aromatic hydrocarbon groups having from 1 to 12 carbon atoms, or they are bonded to each other to form a substituted or non-substituted cyclic compound, comprising the vinyl carbon atom in a ring containing from 3 to 8 carbon atoms, and

(B) a compound of a metal M selected from the group consisting of transition metals and lanthanides, which can be used either as the catalyst, or as a precursor of a catalyst capable of polymerizing ethylene in the absence of the foregoing (A) component, which is constituted by, or is obtained from, an organometallic derivative of said metal M, which contains from 50 to 100% of metal M bonded to an organic residue by means of at least a covalent π -bond;

in such a way that the ratio between the moles of said alpha-olefin of formula (II) and the gram-atoms of said metal M is equal to, or higher than, 2, preferably is comprised within the range of from 50 to 500.

22. Process according to claim 21, in which, besides (A) and (B) components, a third (C) component is placed into contact with them, which is constituted by an alkyl derivative of a metal M' selected from alkali metals, alkaline-earth metals, aluminium, gallium or tin.

23. Process according to claim 22, wherein said (C) component is an aluminoxane and said component (B) is an organometallic derivative of metallocene type.

24. Process according to claim 22, wherein said (C) component is an alkyl derivative of aluminium in which each alkyl residue bonded to aluminium independently contains from 1 to 8 carbon atoms, and said (B) component is a metallocene or a π -allyl derivative of metal M.

25. Process according to anyone of the preceding claims from 21 to 24, wherein said (A) component is placed into contact with the (B) component, or with the resulting product from (B) and (C), at temperature values comprised within the range of from -50°C to $+150^\circ\text{C}$, during a time period long enough in order to obtain the desired activation.

26. Process according to claim 25, in which the contact time is comprised within the range of from 2 seconds to 5 minutes.

27. Process for improving the activity of a catalyst of for ethylene (co)polymerization, constituted by, or derived from, an organometallic compound of a metal M selected from the group consisting of transition metals and lanthanides, which compound contains from 50 to 100% of metal M bonded to an organic residue by means of at least a covalent π -bond, characterized in that said catalyst is placed into contact with an alpha-olefin having the above formula

(II) of claim 1, in such amounts that the ratio between the moles of alpha-olefin and the gram-atoms of metal M is not lower than 2, and preferably is comprised within the range of from 50 to 500.

5 28. Process for ethylene (co)polymerization, comprising feeding and cause ethylene to (co)polymerize in suspension, in solution or in gas phase, in a continuous or batchwise reactor, in the presence of a suitable catalyst, characterized in that said catalyst is the catalyst according to anyone of the preceding claims from 1 to 20.

29. Process according to claim 28, for ethylene homopolymerization.

10 30. Process according to one of the preceding claims from 28 to 29, in which said catalyst is formed in situ in said polymerization reactor.

31. Process according to claim 30, wherein ethylene is fed to the reactor mixed with an alpha-olefin having the above formula (II) of claim 1.



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 96 10 6289

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. CL. 6)
P, X	US-A-5 416 179 (WELCH BRUCE M.) 16 May 1995 * the whole document *	1-3, 5-9, 13-17, 28-30	C08F10/02 C08F4/607 C08F4/611
X	CHEMICAL ABSTRACTS, vol. 73, no. 16, 19 October 1970 Columbus, Ohio, US; abstract no. 77712y, MATKOVSKI: "Activation of the homogeneous catalytic system..." page 77716; column 2; XP002009664 * abstract * & VYSOKOMOL SOEDIN SER A, vol. 12, no. 7, 1970, ---	1-3, 5, 6, 8, 9, 12, 16-18, 28-30	
X	EP-A-0 575 875 (SPHERILENE) * page 13; example 33 *	1-3, 5-7, 9, 12-14, 16-18, 28-30	TECHNICAL FIELDS SEARCHED (Int. CL. 6) C08F
A	FR-A-1 265 836 (OLIVIER M.) * page 1, column 1, paragraph 1 * * page 2, column 2, paragraph 2 - page 3, column 1, paragraph 3 * * claims 1, 2, 4, 5 * * tables IV, VIII, XV *	1	
A	US-A-4 665 047 (SLAUGH LYNN H.) * the whole document *	1	
A	FR-A-1 447 837 (EASTMAN KODAK COMPANY) * example 2; table I * * claims 1A, E, G * * page 1, column 2, paragraph 2 - page 2, column 2, paragraph 2 * --- -/--	1	
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 30 July 1996	Examiner Fischer, B
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		I : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons A : member of the same patent family, corresponding document	

EP 0 FORM 1501 (01/95) (P/0400)

EUROPEAN SEARCH REPORT

Application Number
EP 96 10 6289

DOCUMENTS CONSIDERED TO BE RELEVANT		CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim
A	EP-A-0 002 521 (PHILLIPS) * claim 1 * * column 7, paragraph 2 * * page 16; example 2; table I * * (2) analysis; page 17 * -----	1
		TECHNICAL FIELDS SEARCHED (Int.Cl.6)
The present search report has been drawn up for all claims		
Place of search	Date of completion of the search	Examiner
THE HAGUE	30 July 1996	Fischer, B
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-verbatim disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document		